STANFORD UNIVERSITY LIBRARY
APR 28 1931

GASEOUS EXPLOSIONS

The Effect of Tetraethyl Lead, Hot Surfaces, and Spark Ignition on Flame and Pressure Propagation in Explosive Mixtures

---

By
Mott Souders, Jr.

LC

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE UNIVERSITY OF MICHIGAN

ANN ARBOR
1929

STANFORD UNIVERSITY LIBRARIES
WITHDRAWN

781
625
CLASSED
sertation

Gaseous Explosions

VIII—Effect of Tetraethyl Lead, Hot Surfaces, and Spark Ignition on Flame and Pressure Propagation[1]

Mott Souders, Jr., and Geo. Granger Brown

UNIVERSITY OF MICHIGAN, ANN ARBOR, MICH.

The effect of tetraethyl lead, both in the vapor phase and thermally decomposed, on flame-speeds and rate of rise of pressure following ignition, was determined for explosive mixtures of benzene, pentane, isohexane, and heptane in air. Tetraethyl lead vapor was ineffective in retarding combustion until decomposed by the burning mixture, whereas decomposed tetraethyl lead, introduced before firing the charge, retarded both flame-speed and rate of rise of pressure.

A hot surface was introduced into the bomb to secure auto-ignition of the charge ahead of the advancing flame. This auto-ignition produced an unusually high rate of rise of pressure.

Decomposed tetraethyl lead prevented or delayed the auto-ignition and retarded the resulting combustion.

High-frequency pressure waves ordinarily present in the explosions were eliminated by decreasing the number of sparks in the igniting discharge. The effect of these waves on the combustion and on the initiation of a violent "shock wave" was determined.

ACCORDING to an earlier paper (*2*) the rate of rise of pressure and the auto-ignition temperature of the explosive mixture appeared to indicate the relative knocking tendencies of different fuels in internal-combustion engines. The effect of tetraethyl lead upon rate of rise of pressure was reported a month ago (*3*).

[1] Presented before the Division of Gas and Fuel Chemistry at the 78th Meeting of the American Chemical Society, Minneapolis, Minn., September 9 to 13, 1929.

Last year (*12*) an apparatus was described in which flame and pressure propagation might be investigated. At that time the pressure waves frequently observed in gaseous explosions were shown to be initiated in the inflamed mixture behind the flame front. The influence of such pressure waves on combustion has been indicated by Dixon (*5*). Morgan (*17*) and, more recently, Maxwell and Wheeler (*15*) have suggested that these pressure waves are definitely related to engine knock.

Auto-ignition by adiabatic compression (*1*, *6*, *20*) and ignition of the compressed explosive mixture ahead of an advancing piston (*6*, *8*) or flame front (*23*) at high initial temperature and pressure have been studied photographically. But heretofore no attempt has been made to obtain simultaneous flame photographs and pressure records of auto-ignition induced by a "hot spot" ahead of an advancing flame front initiated by a spark. Moreover, in view of the inconsistencies in the literature, a study of the action of tetraethyl lead and its decomposition products on auto-ignition by a hot spot, on flame speeds, and on rate of rise of pressure seemed desirable. Finally, the effect, origin, and possible control of the high-frequency waves usually present in gaseous explosions initiated by a spark could be investigated in conjunction with the studies on auto-ignition and the effect of tetraethyl lead by use of the apparatus described by Hunn and Brown (*12*).

Apparatus

The apparatus used was essentially the same as that described by Hunn and Brown (*12*), except for the following improvements and additions:

Pressure Element Lamps—The original pressure-element lamp bulbs were found to be too short-lived. After some experiment and upon the suggestion of H. W. Corzine, of the Incandescent Lamp Department of the General Electric Company, type C-8, 6-volt, 18-ampere, projection lamps were adopted. These have been very satisfactory.

Mirror Support—The pressure-element mirror support was redesigned to reduce friction and looseness in bearings. The steel spring originally serving as a bearing support for the mirror axis was replaced by an adjustable pivot and jewel arrangement, shown in Figure 1. To reduce friction and play still further, the V-notched brass wing of the mirror mounting, into which was fitted the slotted pressure rod, was replaced by two small parallel rods, slightly curved downward, and inserted between and bearing upon similar rods which were fastened to the pressure rod by an adjustable screw. Thus curved bearing surfaces, adjustable to take up play, were used throughout.

Reflecting Surface—By employing atomic vaporization in a vacuum tube, the concave mirrors were platinum-plated and the difficulties of silvering were eliminated. The re-

flecting surface thus produced was more uniform and permanent than the silver plate previously employed.

Hot Spot—A hot spot was introduced into the end of the bomb opposite the ignition end. This hot spot consisted of a cylindrical brass cup into the bottom of which was screwed a small brass tube wound with chromel wire embedded in alundum cement. The open end of the cup was joined to the threaded metal part of an ordinary spark plug and alundum cement was packed around the brass tube projecting through this plug. (Figure 2) An insulated thermocouple was inserted in the tube so that the junction was in contact with the bottom of the cup. When in place the bottom of the brass cup was flush with the end plate of the bomb. Temperatures up to 900° C. could be attained with a few minutes' heating. An electric fan served to prevent excessive heating of the bomb by the hot spot. When the heating element failed (after 5 to 10 hours' service), the cement was removed, a new heating element was inserted, and the plug and cup were packed with cement as before.

Charging Pipet—A 1-cc. Luer tuberculin syringe graduated in 0.01 cc. was used for charging the fuel. A long needle with a small opening served to spray the fuel into the combustion chamber, promoting vaporization and distribution. The needle passed through a cork fitted into the charging opening to prevent loss from back pressure when the charge was injected.

Calibration

The pressure elements were calibrated, by means of gas pressure in the bomb, against a Bourdon-type gage which had been previously checked against a dead-weight tester.

Photographic Materials

Eastman hypersensitized panchromatic motion-picture film was used for the flame photographs and Eastman recording paper Nos. 1 and 2 for the pressure records.

Fuels and Mixtures

The four fuels used in this investigation were benzene, *n*-heptane, 3-methylpentane, and a mixture containing 68.8 per cent (by weight) *n*-pentane and 31.2 per cent methylbutane. Their physical properties are given in Table I.

Table I—Properties of the Fuels Used

Fuel	Composition	Boiling Point °C.	$d^{20°}_{4°}$	n_d^{20}
Benzene	C. P.	80.0	0.8774	1.5022
n-Heptane	C. P.	98.2	0.6834	1.3868
Isohexane	3-methylpentane, trace of pentanes	62–64	0.6678	1.3778
Pentane	68.8% *n*-pentane, 31.2% 2-methylbutane, trace of butanes	...	0.6293	....

The benzene was secured from the J. T. Baker Company, chemically pure and thiophene-free.

The *n*-heptane was obtained from the Ethyl Gasoline Corporation and was fractionated further in a standard column. Analysis in a column such as described by Podbielniak (*21*) showed no detectable amounts of other hydrocarbons.

The hexane and the mixture of pentanes were natural-gasoline fractions supplied by the Phillips Petroleum Company. Fractional distillation analyses of the hexane indicated practically pure 3-methylpentane with a trace of pentanes present. Similar analysis of the pentane mixture showed 68.8 per cent (by weight) *n*-pentane, 31.2 per cent methylbutane, and a trace of lighter hydrocarbons.

The tetraethyl lead was obtained through the courtes of the Ethyl Gasoline Corporation, according to whose analysis it contained 98.5 per cent $PbEt_4$. The commercial Ethyl fluid was not used.

Explosions of hydrocarbon-air mixtures of these fuels containing about 20 per cent excess fuel give the maximum

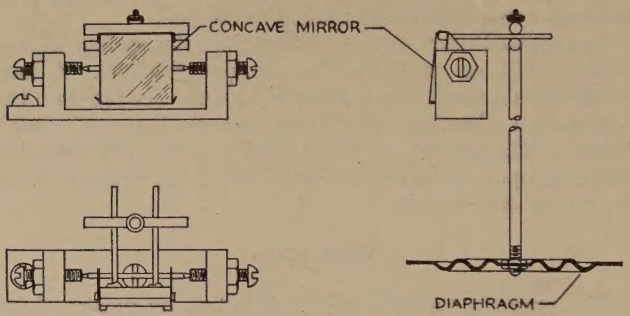

Figure 1—Mirror Mounting

pressure and rate of inflammation. Because mixtures containing about 35 per cent excess fuel produce more actinic explosions, yet differ but little in pressure rise and flame speeds from the maximum-pressure maximum-speed mixtures (*14*), these richer explosive mixtures were used. The initial conditions in all cases were atmospheric pressure and room temperature.

Procedure

The operation of the apparatus and the method of aligning the flame and pressure records have been described by Hunn and Brown (*12*). The new method of charging the fuel and the introduction of decomposed tetraethyl lead, however, require some explanation.

After injecting the fuel into the explosion chamber by means of the syringe described above, 5 to 10 minutes were allowed for vaporization and diffusion before exploding the mixture. This period also allowed sufficient time for placing the film and paper on the drums. That the fuel was completely vaporized and throughly diffused is evidenced by identical records obtained with widely differing diffusion

periods. Moreover, the theoretical partial pressure of the fuel vapor in the mixture was, in the case of heptane, less than 43 per cent of its vapor pressure at the charging temperature. With pentane the partial pressure was 5.9 per cent of the vapor pressure, with 3-methyl pentane 12.7 per cent, and with benzene 27.7 per cent.

Tetraethyl lead was decomposed by dropping the liquid onto the surface of a glass bulb heated electrically to a red heat. An outlet tube from the bulb was inserted in the bomb and the violence of the decomposition served to distribute the decomposition products in the combustion chamber. The decomposed tetraethyl lead was introduced after the diffusion period and the charge was fired immediately afterward.

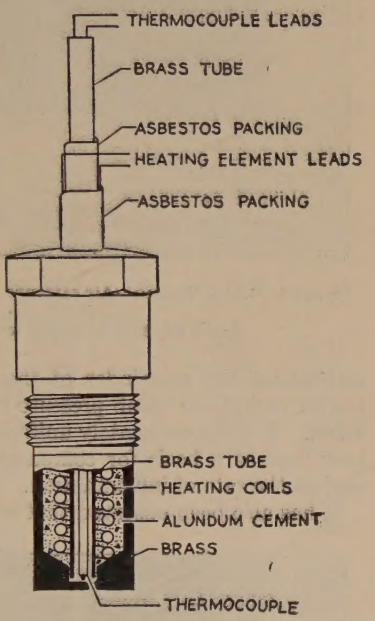

Figure 2—Hot Spot

Elapse of several minutes between introduction of the decomposed tetraethyl lead and firing of the charge apparently rendered the decomposition products ineffective, although a Tyndall effect from the glowing hot spot indicated that the smoke had not settled out.

Undecomposed tetraethyl lead was charged in solution with the fuel. That the tetraethyl lead was vaporized and well distributed is shown by the uniformly increased luminosity of these explosions.

Discussion of Results

Extracts from the experimental data are presented in the accompanying tables.

For convenience in discussion, tetraethyl lead charged in solution with the fuel will be referred to as "undecomposed" and the products of decomposition blown into the bomb with the charge will be called "decomposed."

Flame Speeds and Rate of Pressure Rise—In the investigation of the effect of tetraethyl lead on rate of inflammation and rate of rise of pressure (Table II), the pressure waves were eliminated, by a method described later, in order to exclude their influence on flame and pressure propagation.

From photographs (Figures 3 to 11) of the various hydrocarbon-air mixtures exploded under initial conditions of one

atmosphere and room temperature, it appears that the flame front passes through the charge with an accelerating velocity until about two-thirds of the charge has been inflamed. At this point the flame speed is checked and the inflammation proceeds at a nearly uniform rate (referred to the bomb)

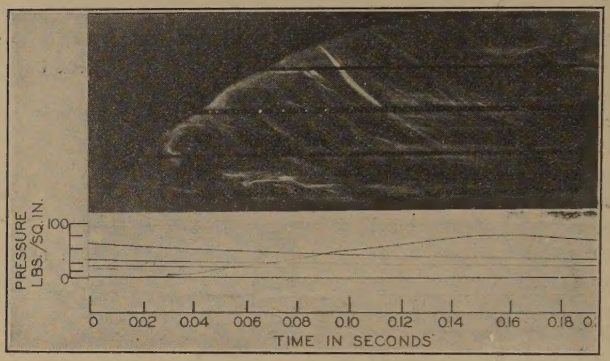

Figure 3—3.51% Benzene-Air Mixture Alone, under 1 Atmosphere at 25° C.
Spark adjusted to reduce waves; no hot spot

throughout the remainder of the unburned charge, unless the far end of the bomb pressure waves again accelerate the flame. This approximately uniform velocity of the flame has been used as a basis for comparing the effect of tetraethyl lead on the rate of inflammation.

It has also been observed that combustion is not complete

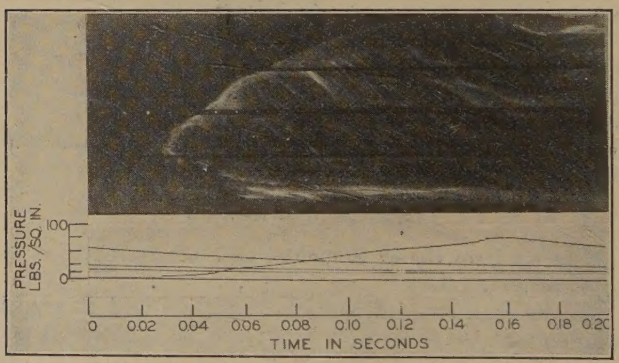

Figure 4—Effect of Tetraethyl Lead Vapor on Flame-Speed. 3.51% Benzene-Air Mixture with 5% Tetraethyl Lead Vapor
Spark adjusted to reduce waves; no hot spot

in the flame front, as there is an appreciable increase of pressure after the flame front strikes the end plate. Data concerning the effect of tetraethyl lead on this rate of pressure rise have also been obtained.

Effect of Tetraethyl Lead Vapor. Although the final, uni-

form flame velocities of the hydrocarbon-air explosions with tetraethyl lead vapor present differ from those of the explosions without tetraethyl lead by an amount less than the experimental error (about 5 per cent), averaging a large number of explosions, indicates a consistent tendency toward decreased flame velocity in the presence of tetraethyl lead vapor. Moreover, the average decrease in the final, uniform flame velocity is much greater than the average increase in the time required for total inflammation. This indicates that any effect of tetraethyl lead vapor is more pronounced in the later stages of the explosion, where higher temperatures and pressures prevail.

Table II—Average Rate of Inflammation and Average Mean *dP/dt* Following Complete Inflammation

Fuel in Mixture %	$PbEt_4$	Av. Final Uniform Vel. of Flame *Cm./sec.*	Av. Time of Total Inflammation *Seconds*	Av. Pressure Rise Following Complete Inflammation *Lbs.*	Av. Mean *dP/dt* Following Complete Inflammation *Lbs./sq. in./sec.*	Waves
			BENZENE-AIR MIXTURES			
3.51	None	206	0.136	8	4308	None
	Vapor	198	0.137	6.5	3293	None
	Decomp.	180	0.155	8	4320	None
			HEPTANE-AIR MIXTURES			
2.61	None	174	0.155	7.5	3420	None
	Vapor	175	0.155	4	2526	None
	Decomp.	152	0.194	2.5	3480	None
			HEXANE-AIR MIXTURES			
2.8	None	153	0.170	7	2530	None
	Vapor	148	0.173	4.25	1905	None
	Decomp.	125	0.212	5	2030	None
			PENTANE-AIR MIXTURES			
3.32	None	162	0.163	9.5	3345	None
	Vapor	157	0.165	6	2105	None
	Decomp.	146	0.190	8	2830	None
			BENZENE-AIR MIXTURES			
3.51	None	205	0.136	8.5	5320	Slight
	Vapor	200	0.135	7	2470	Slight
	Decomp.	176	0.158	7.5	2550	Slight
			HEPTANE-AIR MIXTURES			
2.61	None	196	0.142	11.5	4300	Slight
	Vapor	184	0.150	7.5	3300	Slight
	Decomp.	160	0.178	8	4250	Slight
			HEXANE-AIR MIXTURES			
2.8	None	148	0.171	8.5	2992	Slight
	Vapor	146	0.170	4.9	2090	Slight
	Decomp.	125	0.200	3.5	2575	Slight
			PENTANE-AIR MIXTURES			
3.32	None	160	0.160	9.5	4240	Slight
	Vapor	157	0.163	5	2850	Slight
	Decomp.	144	0.191	8.5	2018	Slight

In all cases the rate of rise of pressure following complete inflammation is greatly lowered when tetraethyl lead vapor is introduced with the fuel, this decrease often exceeding 33 per cent. This effect is more pronounced with the paraffin hydrocarbons than with benzene.

Effect of Decomposed Tetraethyl Lead. The decomposition products of tetraethyl lead greatly retard the velocity of the flame front in all the hydrocarbon-air mixtures studied.

(Table III) In general, decomposed tetraethyl lead also decreases the rate of rise of pressure following complete inflammation, although this effect is not without exceptions. An explanation of the apparent inconsistency is given later.

AUTO-IGNITION—From the pressure curves obtained with explosions of the hydrocarbon-air mixtures under investigation, it appears that the velocity of flame travel and the rate of rise of pressure resulting from auto-ignition by a hot spot ahead of the flame front initiated by a spark are from three to five times as great as the corresponding normal rates at the same stage of the explosion. Auto-ignition in this manner results in an unusually high rate of release of energy. Temperature of the hot spot, apparently, has a greater effect on the rate of rise of pressure than on the velocity of the auto-ignition flame.

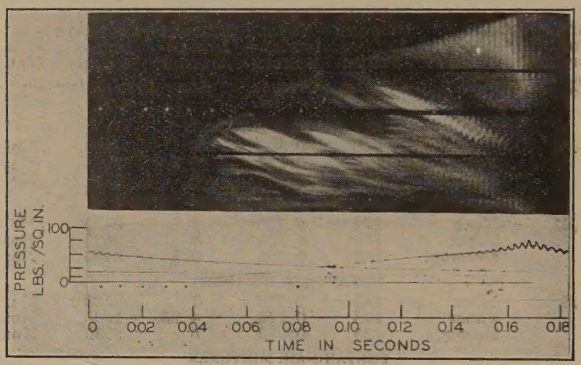

Figure 5—Effect of Decomposed Tetraethyl Lead on Flame-Speed. 3.51% Benzene-Air Mixture with 5% Decomposed Tetraethyl Lead

Spark adjusted to produce violent waves; no hot spot

With initial conditions of atmospheric pressure and room temperature, a red heat was required to secure auto-ignition far enough ahead of the advancing flame front that the auto-ignition flame might have sufficient duration to be accurately measured. Incidental experiments indicated, as would be expected, that increase in the initial temperature or pressure of the explosive mixture permitted auto-ignition with lower temperatures of the hot spot. All data reported here are for initial conditions of atmospheric pressure and room temperature.

Auto-ignition of pentane required a temperature of the hot spot near the maximum attainable with the apparatus. Heptane auto-ignited consistently with a somewhat lower temperature, and 3-methylpentane at a considerably lower temperature than that required for pentane. Benzene could not be made to auto-ignite under any conditions used in this investigation.

Table III—Effect of Tetraethyl Lead on Auto-Ignition

(Initial pressure, 1 atmosphere)

Fuel in Mixture (by Vol.) %	Air-Fuel Ratio (by Wt.)	Initial Temp. °C.	Explosion No.	Temp. Hot Spot °C.	$PbEt_4$ in Fuel	Pressure at Time of Auto-Ignition Lbs.	Length of Unburned Gas Column at Time of Auto-Ignition Cm.	Pressure Waves
HEPTANE-AIR MIXTURES								
2.61	10.7:1	25	241	750[a]	None	No auto-ignition		None
			242	740	None	62	6	None
			243	740	None	No auto-ignition		None
			176	750	None	58	8	Slight
			105	745	5.0 V[c]	No auto-ignition		None
			244	770[b]	None	59	12	None
			248	770	None	59	6	None
			107	770	None	61	6	None
			101[a]	770	None	63	7	Slight
			233	770	None	55	10	Slight
			175	770	None	..	8	...
			303	776	None	63	4	None
			309	780	None	58	6	Slight
			306	783	None	57	6	Slight
			221	788	None	..	8	...
			222	788	None	58.5	6	None
			302	760	0.5 V	66	4	None
			106	770	5.0 V	65	8	Slight
			307	783	0.5 V	55	4	None
			108	785	5.0 V	60	8	Slight
			174	770	0.5 D[d]	60	2	None
			245	770	0.5 D	60	2	Slight
			247	765	5.0 D	No auto-ignition		None
			171	770	5.0 D	No auto-ignition		Violent
			172	770	5.0 D	No auto-ignition		Violent
			173	770	0.5 D	No auto-ignition		None
			234	770	5.0 D	No auto-ignition		None
			235	795	1.0 D	62	2	None
			236	805	1.0 D	66	1.5	None
2.43	11.6:1	25	277	764	None	62	5	Waves
			279	763	None	60	7	None
			276	764	5.0 V	60	4	Slight
			778	760	5.0 V	61	6	Waves
			257	765	5.0 D	No auto-ignition		...
			256	770	5.0 D	No auto-ignition		...
			253	800	None	53	12	None
			254	805	5.0 D	64	14	None
			255	808	5.0 D	62	12	None
HEXANE-AIR MIXTURES								
2.8	11.6:1	20	221	680	None	57	3	Violent
			222	680	None	No auto-ignition		Violent
			223	680	None	56	3	Violent
			224	680	None	No auto-ignition		Violent
			173	685	5.0 V	52	11	None
			174	685	5.0 V	58	8	None
			225	680	0.5 D	55	2.5	None
			226	680	5.0 D	No auto-ignition		Waves
			228	680	5.0 D	No auto-ignition		Fairly violent
			A10	730	None	50	12	Waves
			B10	730	None	52	12	None
			273	718	None	47	10	Waves
			272	712	5.0 V	54	12	None
			274	715	5.0 V	58	10	None
			213	720	1.0 D	52	3.5	Waves
			214	720	2.0 D	47	4	Waves
			215	720	5.0 D	No auto-ignition		None
			191	800	None	41	6	Waves
			193	800	5.0 D	51	4	Violent
			192	800	5.0 D	No auto-ignition		Violent
PENTANE-AIR MIXTURES								
3.32	11.6:1	20	251	782	None	48	16	Slight
			182	780	None	42	22	None
			184	780	5.0 V[a]	40	22	None
			187	780	5.0 D	No auto-ignition		
			188	780	5.0 D	No auto-ignition		

[a] Temperature of hot spot too low for consistent auto-ignition.

[b] Lowest temperature of hot spot at which consistent auto-ignition was obtained.

[c] V denotes $PbEt_4$ charged as vapor.

[d] D denotes $PbEt_4$ charged decomposed.

Table III—Effect of Tetraethyl Lead on Auto-Ignition (*Continued*)

(Initial pressure, 1 atmosphere)

Fuel in Mixture (by Vol.)	Air-Fuel Ratio (by Wt.)	Initial Temp.	Explosion No.	Temp. Hot Spot	PbEt₄ in Fuel	Pressure at Time of Auto-Ignition	Length of Unburned Gas Column at Time of Auto-Ignition	Pressure Waves
%		° C.		° C.		Lbs.	Cm.	
PENTANE-AIR MIXTURES								
			223	794	None	54	6	Violent
			224	790	None	50	6	Violent
			C10	800	5.0 D	No auto-ignition		Violent
			252	812	None	48	16	Slight
			227	820	None	46	8	Slight
			225	830	5.0 D	48.5	4	Violent
			226	835	5.0 D	48	6	Violent

Effect of Tetraethyl Lead Vapor. Tetraethyl lead vapor apparently has little or no effect on either the hot-spot temperature required for, or the flame and pressure propagation

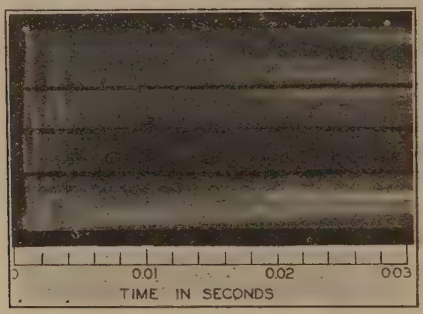

Figure 4—True Detonation Wave, 3% Benzene-Oxygen Mixture, under 1 Atmosphere at 25° C.

Film speed five times as rapid as in other illustrations

resulting from, auto-ignition, under the experimental conditions. It does, however, decrease the rate of rise of pressure after the two flames have merged. It also lowers the rate of rise of pressure after complete inflammation when the temperature of the hot spot is too low to induce auto-ignition.

Effect of Decomposed Tetraethyl Lead. Decomposed tetraethyl lead tends to prevent or greatly delay auto-ignition of heptane, pentane, and 3-methylpentane over a range of hot-spot temperatures of about 40° C. The effectiveness of tetraethyl lead in preventing auto-ignition is less pronounced with 3-methylpentane than with the other fuels. This may be explained by the opportunity for a greater time lag in auto-ignition provided by the relatively lower velocity of the isohexane flame.

With all fuels decomposed tetraethyl lead decreases the speed of the auto-ignition flame and the rate of pressure rise following auto-ignition. (Tables III and IV)

Table IV—Summary of Effect of Tetraethyl Lead on Flame Velocity and Rate of Rise of Pressure Following Auto-Ignition

Fuel in Mixture	Temp. Hot Spot	$PbEt_4$	Vel. of Auto-Ignition Flame	Pressure at Time of Auto Ignition	ΔP after Auto-Ignition	Mean $\Delta P/\Delta t$ after Auto-Ignition	Pressure Waves
%	°C.		*Cm./sec.*	*Lbs.*	*Lbs.*	*Lbs./sq. in./sec.*	
			HEPTANE-AIR MIXTURES				
2.61	770	None	555	60.5	17	7727	None
	776	Vapor	545	60.5	20	8075	None
	790	Decomp.	409	62	10.4	6050	None
	776	None	525	59.5	21	11215	Slight
	785	Vapor	513	62.5	25	14430	Slight
	770	Decomp.	383	60	12.4	6010	Slight
			HEXANE-AIR MIXTURES				
2.8	698	None	793	52	36	11073	None
	698	Vapor	800	56	36	11530	None
	698	Decomp.	549	56.5	31.5	8208	None
	680	None	920	50	22	19165	Violent
	680	Decomp.	594	51	28	11980	Violent
			PENTANE-AIR MIXTURES				
3.32	780	None	717	45	44.5	12150	None
	780	Vapor	726	45	43.5	11900	None
	792	None	693	52	24.2	12115	Violent
	832	Decomp.	309	48	22	9710	Violent

Pressure Waves—The pressure waves normally present in most explosions of hydrocarbon vapors and air travel with a velocity approximately equal to that of sound, and are known to have an accelerating effect on flame speed and rate of rise of pressure (*5*). For this reason it was first thought that these waves might also influence auto-ignition by a hot spot of the unburned gases ahead of the flame. Apparently such is not the case, for auto-ignition was as readily obtained when the waves were eliminated as when they were present.

Maxwell and Wheeler (*15*) stated that these waves were eliminated by decomposed tetraethyl lead but intensified by tetraethyl lead vapor. The results of the present investigation indicate that when the waves exceed an undetermined minimum amplitude the rate of rise of pressure in these waves is increased by tetraethyl lead vapor charged with the fuel. With waves of small amplitudes, however tetraethyl lead vapor decreases the rate of rise of pressure of the combustion induced by these waves. Carr and Brown (*3*) reported a similar effect of tetraethyl lead vapor on the rate of rise of pressure, although because of the limitations of their equipment they made no distinction between the rate of rise of pressure, or rate of reaction, in the normal flame and in the combustion induced by the pressure waves. Perhaps no such distinction is necessary, since the effect of tetraethyl lead vapor appears to be dependent upon the rate of reaction, or rate of rise of pressure, in each case.

It was determined, further, that decomposed tetraethyl lead does not necessarily eliminate these sound-velocity waves, but does invariably suppress or limit their development into a pressure wave of high amplitude or a "shock wave," which sometimes occurs in mixtures not containing decomposed

tetraethyl lead. Apparently the quantity of decomposed tetraethyl lead present is a major factor in limiting the amplitude of the pressure waves.

The sound of the explosion was found to be intimately con-

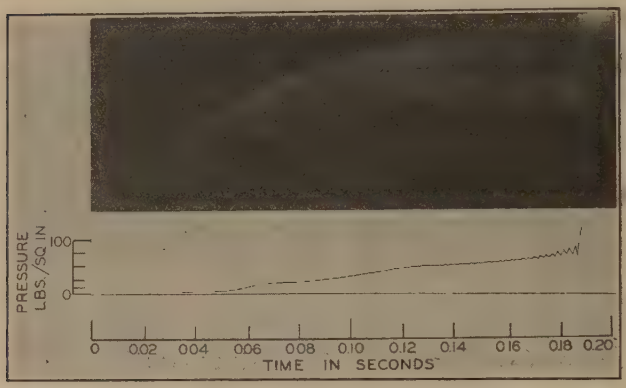

Figure 7—Shock Wave Following Complete Inflammation. 2.8% Hexane-Air Mixture Alone, under 1 Atmosphere at 20° C.
Spark adjusted to produce violent waves; no hot spot

nected with the amplitude of the pressure waves. In silent explosions the waves were absent, and invariably the louder the "ping" the more violent were the vibrations of the pressure indicators.

As Dixon (*5*) and others have suggested that the nature of

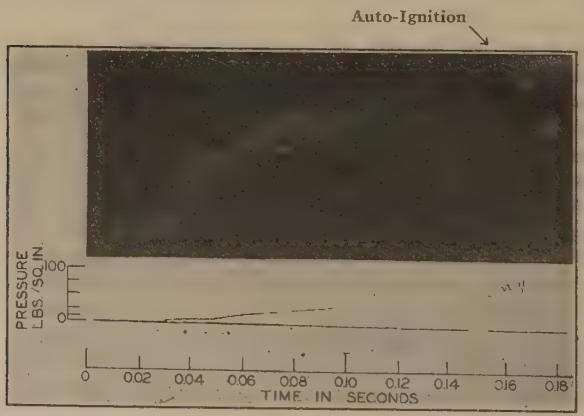

Figure 8—Shock Wave Following Auto-Ignition. 2.8% Hexane-Air Mixture Alone, under 1 Atmosphere at 20° C.
Spark adjusted to produce violent waves; hot spot at 680° C.

the igniting spark is related to the pressure waves, an attempt was made to eliminate these waves by varying the spark. Early experiments to accomplish this result by decreasing the potential across the primary of the spark trans-

former were only partially successful. This procedure resulted in decreasing the amplitude of the waves with all the hydrocarbon-air mixtures used, but it also materially changed the time of total inflammation. Frequently the waves were eliminated entirely, but this result was not consistent.

Further experiments demonstrated that the desired result could be accomplished by shortening the spark-commutator contact. Photographic records made with the camera drum revolving at high speed clearly indicated either that the number of sparks in the discharge was actually decreased by

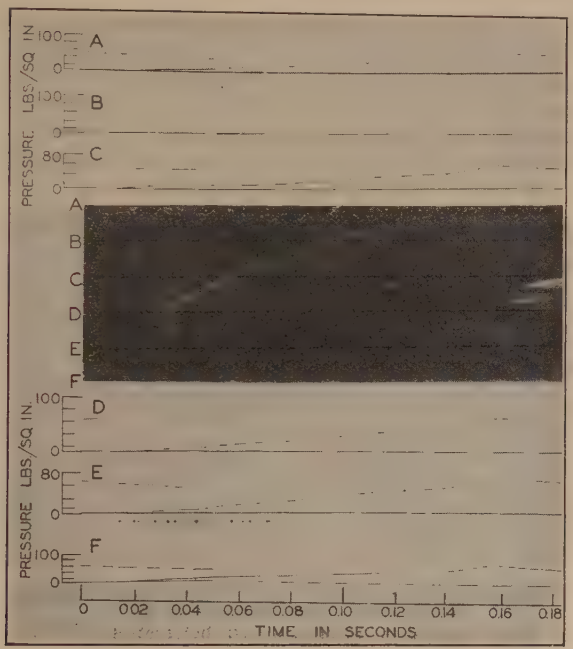

Figure 9—Shock Wave Eliminated by Adjusting Spark to Reduce or Eliminate Pressure Waves. 2.8% Hexane-Air Mixture Alone, under 1 Atmosphere Initial Pressure at 20° C. Hot Spot at 730° C.

Shows the increase in rate of rise of pressure accompanying autoignition but no shock wave or pressure waves.

shortening the spark commutator or at least that the subsequent sparks were of such reduced intensity as to be photographically inactive.

Effect of Tetraethyl Lead

The results of this investigation show that decomposed tetraethyl lead is effective in reducing flame velocity, autoignition, and rate of rise of pressure, but that undecomposed tetraethyl lead is effective only under conditions where decomposition is to be expected. The conclusion that the decomposition products of tetraethyl lead are the effective agents here appears to be inevitable. The suggestion of

Charch, Mack, and Boord (*4*) and of Egerton and Gates (*10*) and the experiments reported by Maxwell and Wheeler (*15*) and by Carr and Brown (*3*) regarding the effectiveness of the decomposition products of tetraethyl lead seem to be confirmed.

Many of the contradictions in the literature concerning the effect of tetraethyl lead on rate of inflammation and rate of rise of pressure are explained by the conclusion that tetraethyl lead must be decomposed to be effective, and that tetraethyl lead vapor accelerates or retards the combustion reactions depending upon conditions.

In the absence of pressure waves undecomposed tetraethyl lead frequently has a more pronounced effect than decomposed tetraethyl lead in decreasing the rate of rise of pressure following complete inflammation. This fact may be explained on the basis of the quantity of effective decomposition products present. The quantity of decomposed

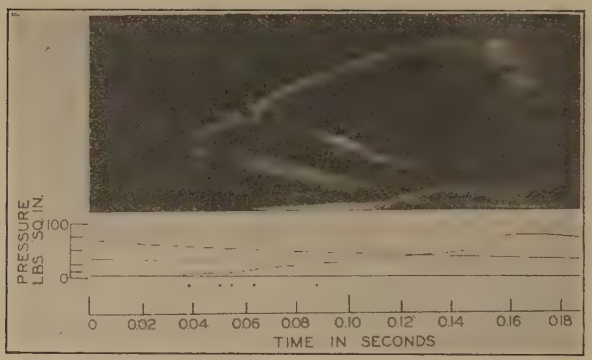

Figure 10—Auto-Ignition. 2.61% Heptane-Air Mixture Alone, under 1 Atmosphere at 25° C.
Spark adjusted to eliminate waves; hot spot at 770° C.

tetraethyl lead charged could not be accurately determined and may have been less than the quantity charged in solution with the fuel, although care was taken to decompose and charge an amount equal to that added in solution with the fuel. However, the destruction of the effective decomposition products starts immediately upon their formation, owing either to agglomeration or oxidation, as they are readily oxidizable substances. The decomposed tetraethyl lead begins to lose its effectiveness immediately upon introduction into the combustion chamber. The tetraethyl lead vapor does not begin to decompose or oxidize appreciably until the flame passes through the mixture; and, therefore, when the gases have been completely inflamed, there is present a larger proportion of effective decomposition products to influence the rate of rise of pressure. This would account for the presence of a greater quantity of effective decomposition products,

although the original charges of decomposed and undecomposed tetraethyl lead were equal.

Deficiency of effective decomposition products also probably accounts for the occasional failure of decomposed tetraethyl lead to prevent the formation of the high-amplitude pressure waves.

Egerton and Gates (*10*) reported that the decomposition of tetraethyl lead in the vapor phase, in air, started at 230° C. and was not complete until the tube containing the tetraethyl lead had been heated to above a red heat, when decomposition was completed with a flash of blue flame and the formation of a gray smoke of metallic lead. Egerton (*9*) found that the tetraethyl lead decomposed up to 230° C. was ineffective in retarding the rate of inflammation. Moreover, experiments in connection with the present work indicate that tetraethyl lead decomposed considerably below a red heat is practically ineffective in decreasing flame velocity.

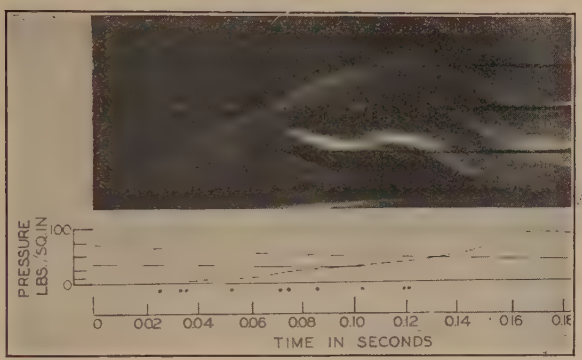

Figure 11—Effect of Tetraethyl Lead Vapor on Auto-Ignition. 2.61% Heptane-Air Mixture with 0.5% Tetraethyl Lead Vapor
Spark adjusted to eliminate waves; hot spot at 770° C.

With these facts as a basis, the effect of undecomposed tetraethyl lead in increasing the already high rate of rise of pressure, when pressure waves are present, whereas decomposed tetraethyl lead decreases this rate of rise of pressure, may be explained by the relative effectiveness of the progressive decomposition products and the rate of decomposition of tetraethyl lead as compared with the rate of inflammation. If the initial decomposition of tetraethyl lead vapor is accomplished by the flame front and the final explosive decomposition is not completed until somewhat later in the combustion, the decomposition of the tetraethyl lead itself (present as 5 per cent of the fuel, by volume) may contribute, as suggested by Carr and Brown (*3*), to the violence of the pressure waves. Or more probably, the primary decomposition products may have a catalytic action as the oxides of lead and particularly the free organic radicals formed

from the decomposition of tetraethyl lead are known to be active oxygen carriers.

Auto-Ignition

Auto-ignition is preceded by a "pre-flame" combustion producing heat more rapidly than it is dissipated, so that, after a sufficient time interval or "lag," the system becomes heated to the temperature at which it bursts into flame (*13*, *22*). Also, lowering the temperature of the gases increases the time lag of auto-ignition (*7*). The action of decomposed tetraethyl lead in preventing or delaying auto-ignition under the conditions of this investigation is believed to be due to dissipation of energy by the decomposed tetraethyl lead during the pre-flame combustion with a consequent lengthening of the time lag.

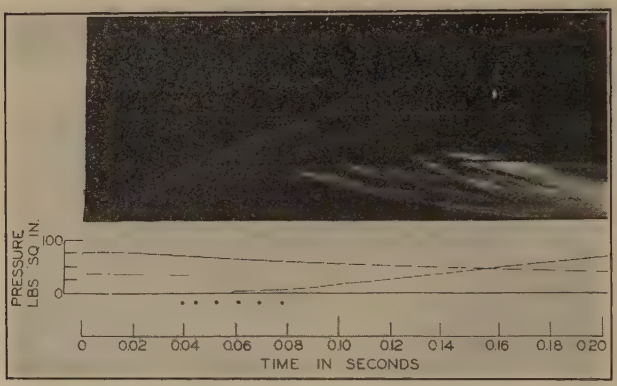

Figure 12—Auto-Ignition Prevented by Decomposed Tetraethyl Lead. 2.61% Heptane-Air Mixture with 5% Decomposed Tetraethyl Lead

Spark adjusted to eliminate waves; hot spot at 770° C.

The rate of rise of pressure finally attained following auto-ignition is dependent, in a large measure, upon: (1) the length of the column of unburned gases through which the auto-ignition flame may travel with an accelerating velocity; (2) the direct effect of the rate of compression (*6*)—i. e., velocity of the original progressive flame; (3) the pressure and temperature at the time of auto-ignition, directly affecting rate of inflammation and after-burning; and (4) rate of compression of the unburned gases between the two flames.

The length of the column of unburned gases at the time of auto-ignition is influenced in turn by: (1) the amount of compression required to raise the gases to their temperature of ignition; (2) the progress of the original flame during the lag of auto-ignition, in turn affected by the inter-relation of velocity of original flame and decrease in lag because of increased compression ahead of the original flame. The interdependence of many of the factors influencing auto-ignition indicates the complexity of this phenomenon.

In this investigation the average rate of rise of pressure following auto-ignition was found to be from three to five times the normal rate. Woodbury, Lewis, and Canby (*23*) observed a high rate of rise of pressure from the auto-ignition of ether-air mixtures. Petavel (*19*) and Fenning (*11*) obtained pressure curves showing an abnormally high rate of rise of pressure and suggested auto-ignition as the cause. In general, it may be concluded that auto-ignition of gases compressed ahead of an advancing flame front results in an unusually high rate of rise of pressure.

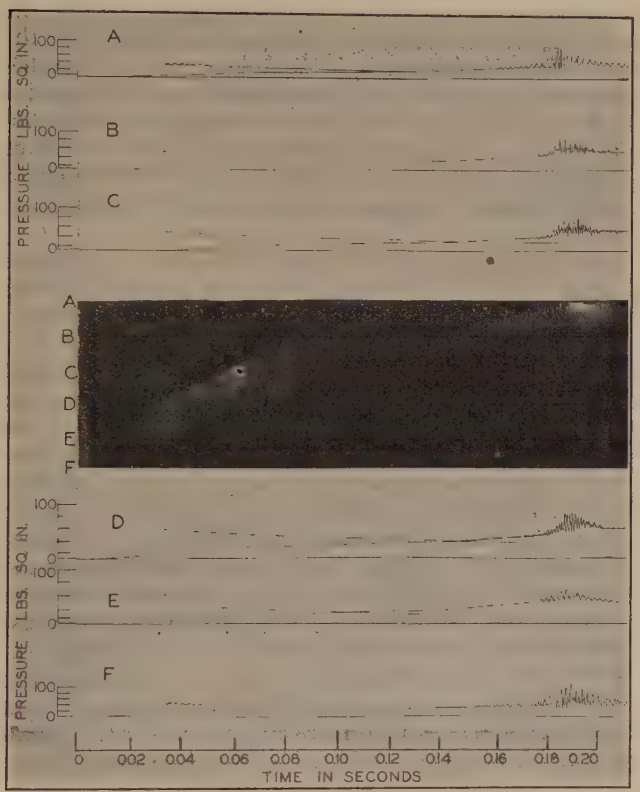

Figure 13—Pressure Distribution when Rate of Energy Release Was Almost but Not Quite Sufficient to Cause Pressure Waves to Develop a Shock Wave Following Complete Inflammation

Pressure Waves

The high-tension induction coil used for ignition in this investigation produces an oscillatory discharge consisting of a series of sparks. Morgan (*16*) and Paterson and Campbell (*18*) have demonstrated that the igniting power of such a discharge depends solely upon the energy of the first spark, and not upon the total energy in the complete series of oscillations.

In the present investigation decreasing the number of sparks in the discharge eliminated the pressure waves without appreciably changing the speed of the flame up to the point where it begins to accelerate under the influence of the waves. It appears, therefore, that these pressure waves are initiated in the partially burned gases by sparks passing subsequently to the initial, igniting spark, and that reduction or elimination of these superfluous sparks will prevent formation of the waves.

The waves first appear on the pressure records as vibrations of very small amplitude. With each oscillation, however, the amplitude increases, slowly at first but accelerating as the combustion proceeds, until, if the rate of energy release becomes high enough, the amplitude rapidly attains that of a shock wave which ruptures the brass diaphragm of the pressure indicator. Apparently increase in the rate of rise of pressure and increase in the amplitude of the waves exert a mutual influence, increase in one serving to increase the other.

With the paraffins the acceleration of the rate of rise of pressure in and by the waves is very rapid, but with benzene this acceleration is relatively moderate. Shock waves were occasionally observed in explosions of the paraffins even though great pains were taken to prevent their development because of the resulting damage to the apparatus, but shock waves were never developed in explosions of benzene. These facts indicate that the residual energy to be released by combustion after inflammation of benzene-mixtures is less than in paraffin mixtures, as suggested by Maxwell and Wheeler (*15*), or that the after-burning is not influenced to as great an extent by the pressure waves in the benzene mixtures.

With auto-ignition the rate of rise of pressure was often as high as that produced by the high-frequency waves just before the appearance of the shock wave. Auto-ignition, however, did not produce a shock wave unless waves of high amplitude were present. On the other hand, waves of high amplitude did not set up or develop into shock waves unless considerable energy was released by auto-ignition or by the after-burning following normal combustion.

It should be noted that the shock wave observed in the present investigation differs markedly from a true detonation wave. The "shock-wave" is apparently developed only after auto-ignition of the explosive mixture ahead of the flame or after complete inflammation, and is reflected back and forth through the completely inflamed gases with the velocity of sound. The detonation wave is an intense pressure wave passing through the unburned gases with a velocity several times that of a sound wave, and causing intense combustion of the explosive mixture. A true detonation wave is represented by Figure 6 and is included for purposes of comparison.

Conclusions

1—Tetraethyl lead must be decomposed to be effective, at least in explosive mixtures.

2—Decomposed tetraethyl lead decreases flame velocity and rate of rise of pressure, particularly of the auto-ignition flame, and raises the temperature required for auto-ignition ahead of the flame front.

3—The pressure waves are initiated in the partly burned gases by sparks passed subsequently to the initial igniting spark.

4—A shock wave is developed from the mutual influence of pressure waves and a high rate of release of energy.

5—Auto-ignition ahead of the flame front results in a high rate of release of energy.

Acknowledgment

The authors are indebted to Norman S. Banta for his assistance with the experimental work.

Literature Cited

(1) Aubert, Pignot, and Villey, *Compt. rend.*, **185**, 1111 (1927).
(2) Brown and Watkins, IND. ENG. CHEM., **19**, 366 (1927).
(3) Carr and Brown, *Ibid.*, **21**, 1071 (1929).
(4) Charch, Mack, and Boord, *Ibid.*, **18**, 334 (1926).
(5) Dixon, *Trans. Roy. Soc. London*, **200A**, 319 (1903); *J. Soc. Automotive Eng.*, **9**, 237 (1921).
(6) Dixon, Bradshaw, and Campbell, *J. Chem. Soc.*, **105**, 2027 (1914).
(7) Dixon, Harwood, and Higgins, *Trans. Faraday Soc.*, **22**, 267 (1926).
(8) Duchene, *Compt. rend.*, **186**, 220 (1928).
(9) Egerton, *Nature*, **119**, 259 (1927).
(10) Egerton and Gates, *J. Inst. Petroleum Tech.*, **13**, 244 (1927).
(11) Fenning, Rept. Mem. Aeronautic Research Committee, No. 979 (1925); *Engineering*, **121**, 180 (1926).
(12) Hunn and Brown, IND. ENG. CHEM., **20**, 1032 (1928).
(13) Mason and Wheeler, *J. Chem. Soc.*, **125**, 1868 (1924).
(14) Maxwell and Wheeler, *Ibid.*, 2069 (1927).
(15) Maxwell and Wheeler, *J. Inst. Petroleum Tech.*, **14**, 175 (1928); IND. ENG. CHEM., **20**, 1041 (1928).
(16) Morgan, *J. Chem. Soc.*, **115**, 94 (1919).
(17) Morgan, *Phil. Mag.*, [7] **3**, 1161 (1927); *Automotive Eng.*, **15**, 27 (1925).
(18) Paterson and Campbell, *Proc. Phys. Soc.*, **1919**, 177.
(19) Petavel, *Phil. Mag.*, **3**, 461 (1902).
(20) Pignot, *J. usines gaz*, **50**, 293 (1926).
(21) Podbielniak, *Oil Gas J.*, **27**, No. 35, 38 (1929).
(22) Taffanel and LeFloch, *Compt. rend.*, **156**, 1544 (1913); **157**, 469 (1913).
(23) Woodbury, Lewis, and Canby, *J. Soc. Automotive Eng.*, **8**, 209 (1921).